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NEW APPROACH TO CHEMICALLY INDUCED SILICON OXIDATION

FINAL REPORT

DR. RALPH J. JACCODINE

DR. DONALD R. YOUNG

OCTOBER 1, 1991

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER: DAAL03-88-K-0095

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DEPARTMENT OF COMPUTER SCIENCE AND ELECTRICAL ENGINEERING

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13. ABSTRACT (Maximum 200 words) The project "New Approach to Chemically Induced Silicon Oxidation" suggested a new and different approach to oxidation by the addition of small concentrations of a Fluorine compound to the oxidation strain. This novel approach was successfully carried out within the framework of state-of-the-art oxidation technology. The objectives for the study were divided into four sections and the core elements of these sections are further discussed in the attached report. Each of the sections was carried out successfully with objectives reached. Additionally, a great deal of insight and new material was uncovered which solidified the investigators opinion that this process is superior to present state-of-the-art industrial practice. In addition to the reduced (by two orders of magnitude) impurity inclusion for Fluorine sources vs. Chlorine sources, many of the beneficial effects on point defects, traps, MOS quality, etc. are included in this study and make the above statement valid.

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## FORWARD

The project "New Approach to Chemically Induced Silicon Oxidation" suggested a new and different approach to oxidation by the addition of small concentrations of a Fluorine compound to the oxidation strain.

This novel approach was successfully carried out within the framework of state-of-the-art oxidation technology.

The objectives for the study were divided into four sections and the core elements of these sections are:-

Part 1 - Study of oxidation kinetics with original source 1-2

dichlorofluorethane. (Study of temperature, time, volume additions.)

Part 2 - Involves MOS characterization and effect of "hot" carriers.

Part 3 - Influence of this process on stacking faults, furnace ambients and other oxidation related effects.

Part 4 - Investigate use of other compounds for this purpose.

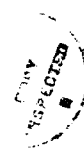
Each of the sections was carried out successfully with objectives reached. Additionally, a great deal of insight and new material was uncovered which solidified the investigators opinion that this process is superior to present state-of-the-art industrial practice. In addition to the reduced (by two orders of magnitude) impurity inclusion for Fluorine sources vs. Chlorine sources, many of the other beneficial effects on point defects, traps, MOS quality, etc. are included in this study and make the above statement valid.

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## 1991 ARO REPORT

The project "New Approach to Chemically Induced Silicon Oxidation" (Preparation and Properties) suggested a new and different approach to oxidation which was aimed at using a chemical additive to the oxidation stream to enhance the rate especially at lower temperature ( $<1000^{\circ}\text{C}$ ). We showed that this approach was feasible by using low concentrations ( $<.1\%$ ) of hydrogenated aliphatic additive (1-2 dichloro-fluorethane) to the oxidation stream.

The objectives in this project were divided into four sections and the core elements are as briefly stated:

Part 1 - Study of oxidation kinetics with original source 1-2

dichlorofluorethane. (Study of temperature, time, volume additions.)

Part 2 - Involves MOS characterization and effect of "hot" carriers.

Part 3 - Influence of this process on stacking faults, furnace ambients and other oxidation related effects.

Part 4 - Investigate use of other compounds for this purpose.

We shall report on each section in turn.

### PART 1 - OXIDATION KINETICS STUDY:-

The first phase of our studies was to adapt "standard equipment" used in industry, i.e horizontal thermal oxidation furnace to be used in the new process. The practical implementation of this process was to use standard high temperature (Mini Brute) furnaces modified with an appropriate gas handling and temperature controlled "bubbler" system capable of mixing the proper flows of impurity to oxidant gases. With this system we established the experimental source, gas delivery system, apparatus and conditions for the study. The work established the growth characteristics of the  $\text{SiO}_2$ , as well as



some of the influence of the amount of fluorine additions on the various growth parameters.

The early phases of this work was established in an M.S. Thesis by C. Wolowodiuk<sup>(1)</sup> later in Ph.D. Thesis by U.S. Kim<sup>(2)</sup>. Some of the most recent work has been summarized by Kim, Wolowodiuk, Jaccodine et al.<sup>(3)</sup>

We have established first, that small amounts of a fluorine source ( $\text{NF}_3$  or  $\text{C}_2\text{H}_3\text{Cl}_2\text{F}$  in the region of .0x/100% - hundredths of a percent) greatly enhances the oxidation rate.

As can be seen in FIGURE 1<sup>(3)</sup>, there is a large enhancement of the dry oxide thickness with fluorine added compared to the other state-of-the-art sources.

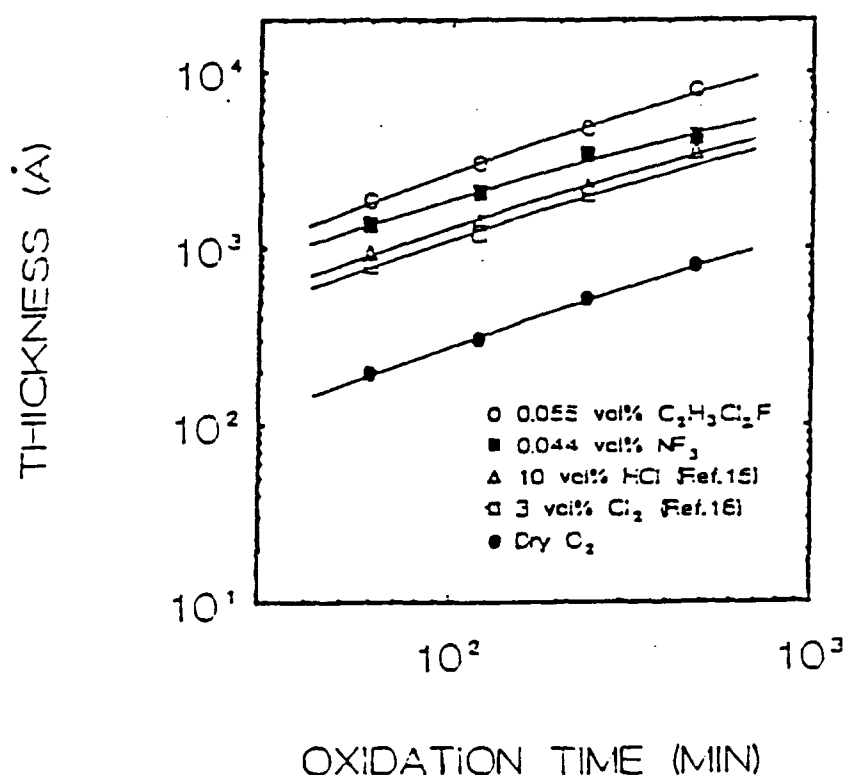


FIGURE 1. Oxide thickness vs. oxidation time for the oxidation of lightly doped silicon in various gas ambients at 1000°C. The points represent the experimental data. Solid line is the least squares fit with the power of time.

other industrial processes, even over that for a ten percent volume addition of HCl with as low an addition of 400 ppm. (by volume) of the Fluorine compound. In this same reference<sup>(3)</sup> is also summarized the effective B and B/A parameters for the Deal-Grove linear-parabolic model as well as the constant for the power of time model as proposed in REFERENCES 4 and 5. These parameters define the relevant growth laws for this process.

One of the key findings of this earlier work, which was anticipated but was even more dramatically demonstrated, was the need for good control over the active Fluorine concentration. "Too much of a good thing" was found to be deleterious. This is a clear indication of the competition between oxide enhanced growth and the tendency for Fluorine species to act as an etchant of the growing oxide.

For the analyses of the growth kinetics previously mentioned, it was shown that Fluorine plays a key role in the structure of the oxide formed, namely the oxide structure was opened sufficiently for the parabolic rate constant (related to oxidant diffusion) to show a marked enhancement. The interface kinetics were also modified indicating that Fluorine acts almost catalytically with a resultant increase in the linear growth rate regime. Another measure of these effects was seen by the effect that F additions have on the dielectric properties and optical index.

The work in this part of the research was also aimed at specific kinetic information on the new processes. We have explored this issue and have discussed the kinetic data in terms of both the more traditional Deal-Grove (linear-parabolic) model<sup>(4)</sup> and also using the power of time model favored by E. Nicollian and A. Reisman.<sup>(5)</sup>

This information is found in tabulation of temperature and fluorine impurity

This information is found in tabulation of temperature and fluorine impurity and concentration in Table II and Table III of REFERENCE 3.

In addition, the resultant inclusion of Fluorine in the  $\text{SiO}_2$  was studied as a function of the two "generic" sources used in the kinetic study by SIMS. It was a finding of this work that the shape of the (F) profile depended on when it was introduced into the growth process, as well as the type of source impurity used. Specifically, these profiles were highly dependent on the "dryness" of the oxidation. It was postulated (to explain this data) that, with hydroxides present, F will move by a replacement reaction similar to that which occurs for Cl. In contrast, with our  $\text{NF}_3$  source and dry oxidation the F profiles are generally quite flat and "saturated" throughout the oxide.

## PART II - ELECTRICAL CHARACTERIZATION OF FLUORINATED OXIDES

An extensive investigation has been made of the charge trapping, charge transport and interface characteristics of fluorinated oxides. The samples used for these investigations have been prepared with the fluorine applied during the oxidation process and by the use of ion implantation after the oxides are grown. We have become increasingly interested in the interface characterization since the modern trends toward thinner oxides makes the interface relatively more important than the bulk characteristics.

To enable us to characterize the interface we have developed a relatively new characterization method called the Q-V method that can be used with MOS (Metal Oxide Silicon) capacitors. This method enables us, with relatively simple straight forward methods, to determine the interface potential. Briefly, we measure the charge developed in the circuit by accurate voltage measurements of the voltage developed across a known reference capacitor. If the charge is known and the oxide capacity is known then we are able to calculate the

voltage across the oxide. Subtracting this voltage from the applied gate voltage gives us the interface potential. Plots of this potential vs. the applied gate voltage give information that can be easily used to obtain the interface state density distribution. We have a new technique to evaluate the "unknown constant" using only the results obtained from this measurement. This enables us to determine the interface potential on an absolute scale and not just a relative scale.

We compare the results with the theoretical predictions using the Kingston Neustadter theory<sup>(6)</sup>. In our case, we use the theory to calculate the interface potential vs. gate voltage and not the capacity as is usually done. The comparison of the results for the "ideal" case with our measured results gives us the interface charge as a function of interface potential. The slope of this curve gives the interface state density distribution.

We have designed our apparatus to be interfaced with a personal computer and this is being routinely used in our laboratory for these investigations. A paper has been completed on our techniques and this will be submitted for publication in the near future. Work on the design and construction of this apparatus has been done by Ta-Cheng Lin and he has made samples and measurements using this technique. In FIGURES 2, 3 and 4, the results obtained by Lin are shown. These samples were n-type, phosphorus doped 100 wafers with a resistivity of 1-2 ohm cm. The oxide is grown in a dry oxidation furnace at 1000°C for 45 minutes resulting in a oxide thickness of 635 Å. After oxidation, the samples are implanted with F at 25 KeV. Three different doses ( $10^{13}$ ,  $10^{14}$ ,  $10^{15}$ )/cm<sup>2</sup> were used. After implantation, the samples are annealed for 30 minutes in a N<sub>2</sub> ambient at 900°C to remove physical damage resulting from implantation. Aluminum gates are deposited in a vacuum chamber

with low sodium contamination. Finally, some of the samples are post metal annealed in forming gas at 450°C for 30 minutes.

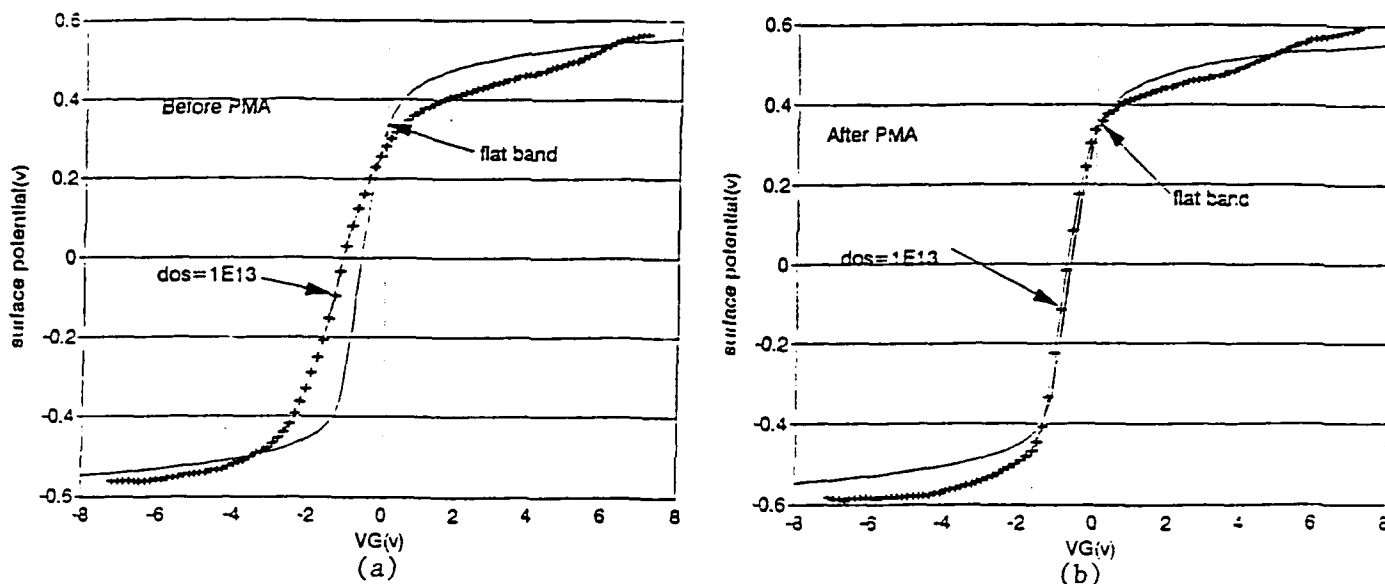


FIGURE 2. Surface potential vs. gate voltage curves for the F implanted oxide (a) before post-metal annealing and (b) after post-metal annealing. (Dos =  $1 \times 10^{13} \text{ cm}^{-2}$ ).

The figures show the experimental measurements and the results of the Kingston Neusdater theory for comparison. The best results are for the sample with a dose of  $10^{14} / \text{cm}^2$ . For this particular sample the flat band voltage was close to zero. The close agreement between the curves shows the small interface state density for this sample. There is interesting structure appearing very close to the conductance band that is present in all samples but has a minimal effect for this case. This suggests the presence of states very close to the conduction band. To be certain that this was not an artifact due to our instrumentation we made similar measurements using a linear capacitor instead of the MOS capacitor. We obtained a straight line as a result which indicated that the apparatus is precisely linear.

We have been anxious to compare samples made by adding the impurities during

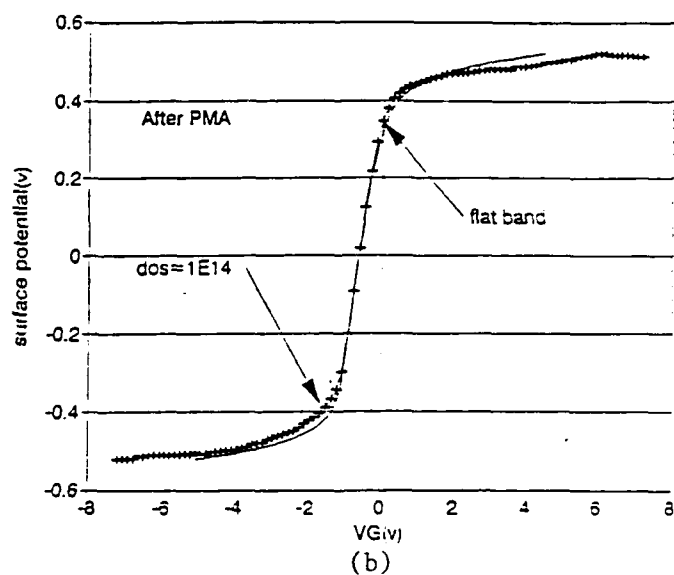
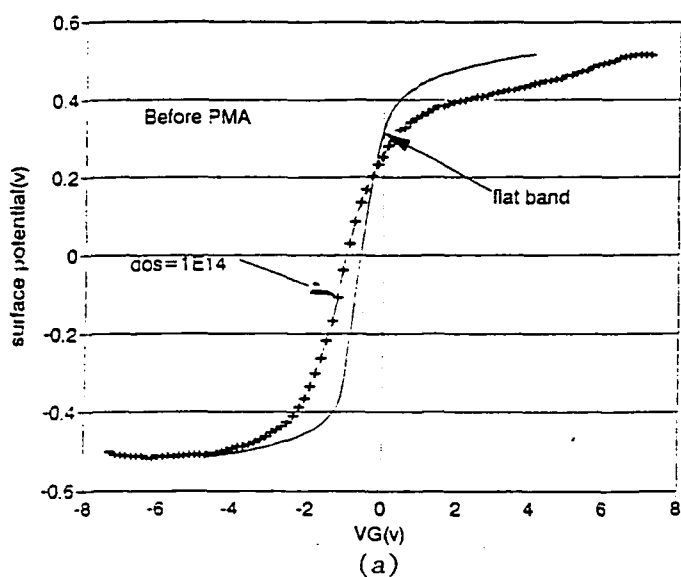


FIGURE 3. Surface potential vs. gate voltage curves for the F implanted oxide (a) before post-metal annealing and (b) after post-metal annealing. ( $Dos = 1 \times 10^{14} \text{ cm}^{-2}$ ).

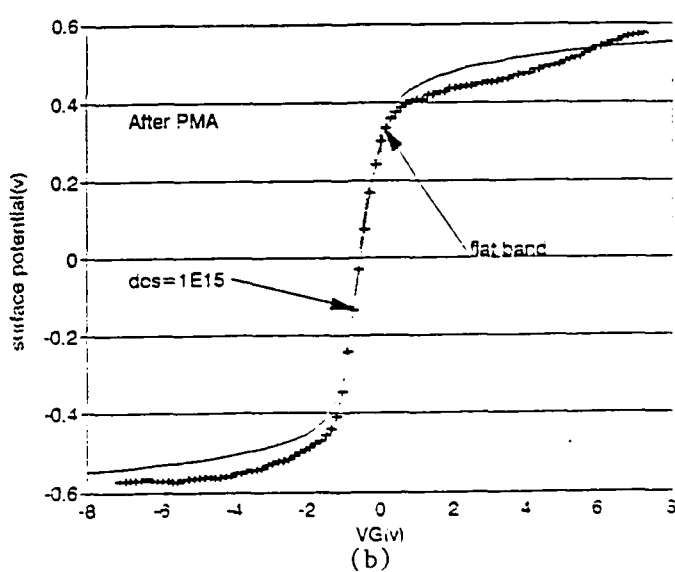
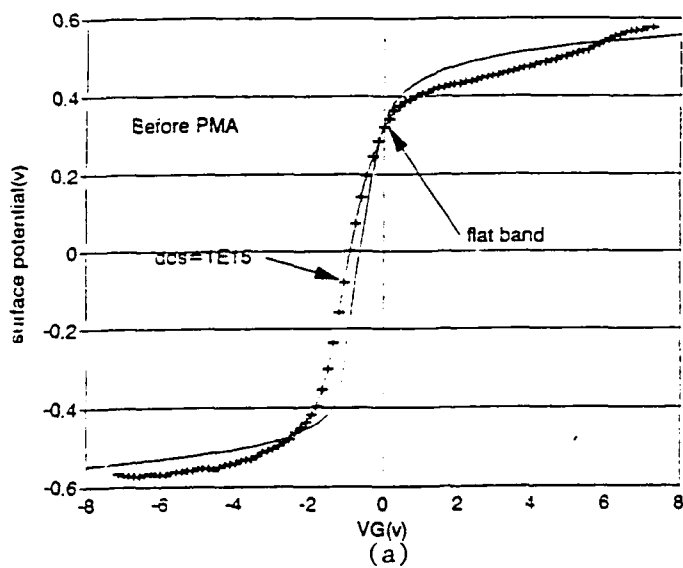


FIGURE 4. Surface potential vs. gate voltage curves for the F implanted oxide (a) before post-metal annealing and (b) after post-metal annealing. ( $Dos = 1 \times 10^{15} \text{ cm}^{-2}$ ).

the. oxidation to those made by the addition of fluorine using ion implantation. The first portion of the work used gaseous sources and we were concerned about the possibility that our observations were due to impurities in the gas sources and not due to fluorine. As a result, we have placed our emphasis on the use of ion implantation. In the latter case there is a concern that our results might be due to implantation damage and not fluorine. We routinely give our samples a heat treatment at 1000°C after the implantation to anneal out this damage. We have also studied samples implanted with inert gases and find that in the context of our measurements there remains only negligible damage. The results for the implanted samples as compared with the non-implanted samples are almost identical. In the case of ion implantation we have an excellent comparison for our studies since we apply the implantation to 1/2 of the wafers and use the other non-implanted portion as a reference.

In addition to the interface characterizations we have also studied the electron trapping characteristics using our automatic apparatus to apply a known electron current to the sample and measure the charge build-up due to the trapped electrons. In concert with these studies we have also studied the build up of slow donor states near the interface in response to the fluence of electrons. In addition our studies include interface state measurements. We have developed methods to separate the effect of the bulk trapped charge, the donor state build up which leads to a positive interface charge and the generation of interface states. This work has been described in a recent publication in the Journal of Applied Physics.<sup>(7)</sup> These results were also described in a paper given at the SISC Conference held in San Diego, December 1990.

A summary of our results is as follows:

The addition of fluorine, whether by gaseous sources or by ion implantation, results in additional electron traps in the oxides that have been characterized. These traps do not have a large trapping cross-section (i.e.  $5 \times 10^{-18} / \text{cm}^2$ ) and therefore would not be of concern with respect to the hot electron problem in operating devices.

In agreement with the observations of others such as da Dilva, Nishioka and Ma<sup>(8)</sup> we have observed that there is a optimum concentration for the fluorine as far as the interface is concerned. These authors studied radiation hardness and in our case we have studied the slow donor state generation. These results are shown in FIGURE 5 taken from Xie's thesis.<sup>(9)</sup> This work

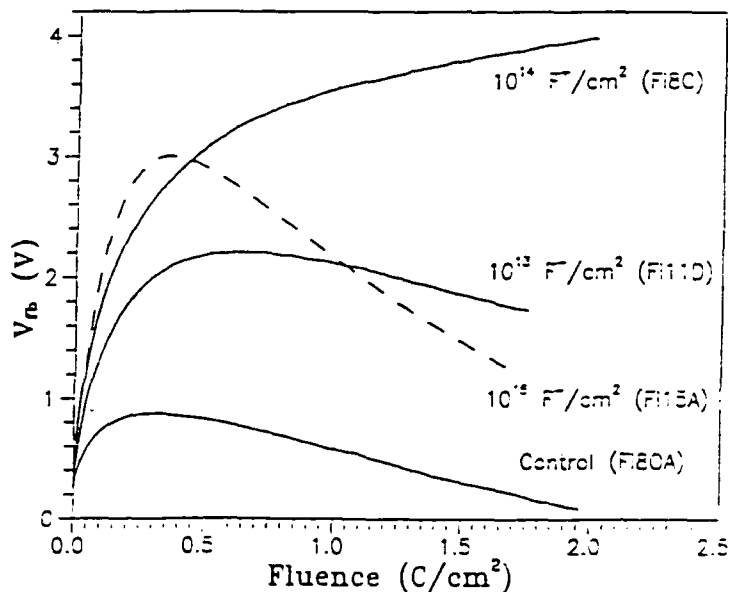


FIGURE 5. Avalanche electron injection at room temperature for control and fluorinated oxides ( $d_{\text{ox}} = 600 \text{ \AA}$ ; current density:  $2 \times 10^{-5} \text{ A/cm}^2$ ). The turn-around effect is shown for all the samples except the sample with an implant dose of  $10^{14} \text{ F}^+ / \text{cm}^2$ .

consisted of passing a known electron current through the oxide and measuring the charge build up using the flat band voltage shift. These results consist of a positive shift due to the trapped electrons in the bulk and a



compensating positive charge (negative charge) at the interface due to the donor states generated. It is seen from the figure that a ion implantation dose of  $1 \times 10^{14}/\text{cm}^2$  essentially eliminates the donor state generation which occurs for larger and smaller doses.

Our first realization that interface states generated by the avalanche injection process were playing a major role came in Xie's work on electron trapping. When he used techniques to eliminate complications due to donor state build up, he observed much larger flat band voltage shifts as compared with mid-gap shifts measured on similar samples. There were two possible explanations for this result. One possibility was that the flat band was correct and that the larger mid-gap shifts were due to the build up of negative charge due to interface states that are charged at mid-gap and not at flat band. Another possible explanation was that the mid-gap values were indeed correct and there was positive charge build up due to the generation of donor states which was compensating the negative charge due to trapped electrons in the bulk. Further investigations showed that the C-V characteristics were translated in a more parallel manner if the measurement was done at an elevated temperature. This temperature anneals out the interface states as they were generated. This clearly showed that the effect was indeed due to donor states generated in the lower portion of the Si energy gap which gave us the positive charge.

### PART III - OTHER PHYSICAL EFFECTS ON PROPERTIES:-

This area covers important "other effects" that are a consequence of or bear on the technology of oxidation. Oxides grown by the new process were examined for any anomalous breakdown or ionic migration behavior. These oxides were shown to be as good as those of the best present practice, and every

indication is that F acts as an efficient materials getter for impurities.

More pertinent, because it represents new findings, is the role F plays in suppressing oxidation induced stacking faults. It was conjectured in our proposed work that fluorine may be able to suppress stacking fault nucleation and growth; in fact, it was extremely effective for this purpose. We investigated the behavior of oxidation induced stacking faults (OSF's) during fluorine-oxidation in temperature range 850°-1100°C. It was observed that pregrown OSF's shrink very rapidly and that no OSF's are generated even when damage is purposely done to the wafers prior to oxidation. This work<sup>(10)</sup> also showed that the activation energy for shrinkage is much lower than for other comparable processes. This is shown by the FIGURE 6 below:

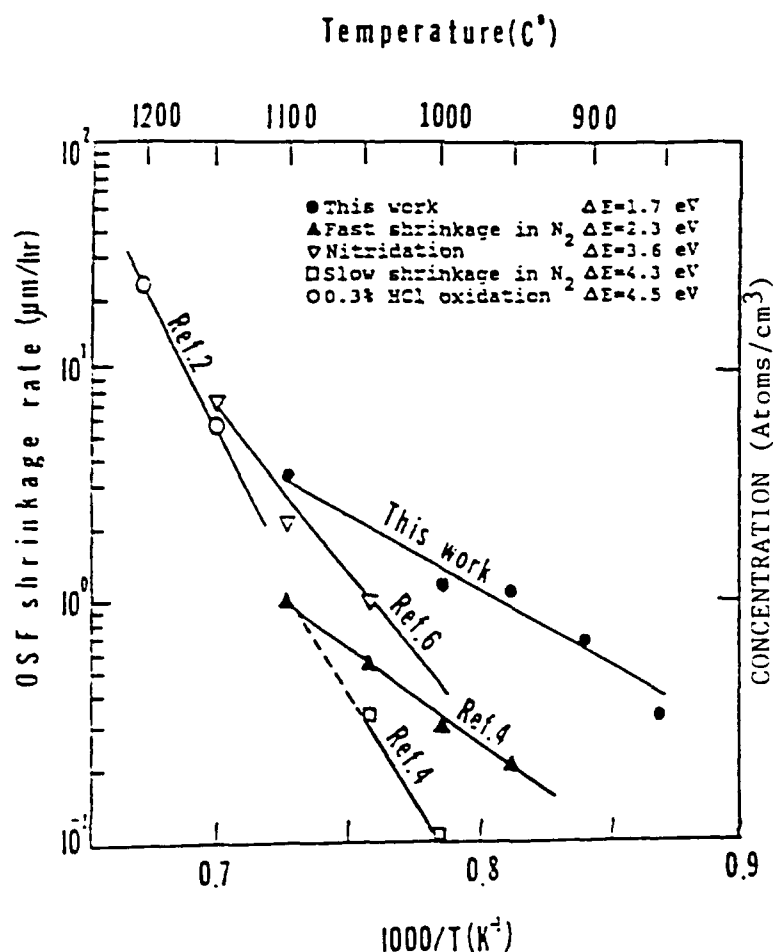


FIGURE 6. OSF shrinkage rates in various thermal heat treatments

The more complete findings of this work are published in Lehigh Ph.D. Thesis by U.S. Kim<sup>(2)</sup>.

One of the unexpected results of this work is that the new F oxidation process completely reverses the normal point defects balance at the growing interface such that vacancies are induced over the equilibrium concentration  $C_v > C_v$  eq. and that these vacancies (instead of interstitial silicon) are injected back into the substrate. The important implication of this is that oxidation enhanced/retarded diffusion effects are reversed over those normally expected. (See Chapters 5 and 6 of REFERENCE 2).

#### PART IV - INVESTIGATION OF THE OTHER COMPOUNDS (PARTICULARLY FREONS) AS SUBSTRATES FOR ADDITIVE VAPOR SOURCE

In this part of the project we anticipated that a few other fluorine containing additives may be also readily useful sources. We also expected that a great deal of trial and error substitution of additive gases would be required. It was quite clear that the original source (Dichlorofluorethane -  $C_2H_3Cl_2F$ ) we selected and used had very convenient handling and vapor pressure properties for easy replacement into a state-of-the-art oxidation facility. This is where the work started. It became also obvious by considering the SIMS profiles of included F in the oxides that the presence of hydrogen in this source resulted in an effective "wet" oxide. This was also seen in growth rate vs. temperature results. Our next step was to investigate a source with neither the H or the CL. This source  $NF_3$  turned out to be the simplest and most flexible and useful of the ones investigated. All the work by Wolowodiuk, Kim, McCluskey and Huang (theses and publications) were carried out using one or other of these two sources.

In order to come to grips with the potential multitude of available Freon-like sources (Freon 11, 14, 22, etc.), we not only explored the literature for current use but importantly we used the SOLGAS program<sup>(11)</sup> to calibrate the partial pressure of possible oxidizing species under the actual high temperature oxidation conditions in the furnace. These calculations could be accomplished for all the reasonable source families that were considered provided sufficient thermodynamic information was available. In that way families of like compounds could be compared to give insight into what species were responsible for enhancing rates, etc. For example, the  $C_2H_3Cl_2F$  dissociates at high temperature and formed many of the same products as trichloroethylene ( $C_2H_3Cl_3$ ) and trichloroethane ( $C_2HCl_3$ ). But there were additional unique species formed from the  $C_2H_3Cl_2F$  source that gave strong indications as to the important actual species partial pressures that were different and thus effective for understanding the process.

This simulation and calculation technique was also employed to explore (theoretically) the role of small additions of  $H_2$  (and, of course,  $H_2O$ ) to the ambient. This approach also allowed us to recognize the advantages of the use of the  $NF_3$  source.

The gas phase comparisons of the two sources used in these studies can be shown in the table of FIGURE 7.<sup>(2)</sup> This can also be seen, perhaps more dramatically, in FIGURE 8<sup>(2)</sup> which is a plot of partial pressure in N-F-O-H cyclic vs. a function of temperature.

By means of these calculations and simulations, many experimental conditions and source compositions could be compared without the need for the large expenditure of effort, materials and cost entailed in one for one comparison experimental work.

O <sub>2</sub> /C <sub>2</sub> H <sub>3</sub> Cl <sub>2</sub> F system		O <sub>2</sub> /NF <sub>3</sub> system	
Chemical Species	Partial Pressure	Chemical Species	Partial Pressure
O <sub>2</sub>	0.99x10 <sup>0</sup>	O <sub>2</sub>	0.99x10 <sup>0</sup>
HCl	0.43x10 <sup>-2</sup>	F	0.51x10 <sup>-2</sup>
HF	0.22x10 <sup>-2</sup>	ONF	0.76x10 <sup>-2</sup>
CO <sub>2</sub>	0.22x10 <sup>-2</sup>	N <sub>2</sub>	0.71x10 <sup>-2</sup>
H <sub>2</sub> O	0.28x10 <sup>-4</sup>	F <sub>2</sub>	0.29x10 <sup>-3</sup>
Cl <sub>2</sub>	0.22x10 <sup>-4</sup>	HF	0.99x10 <sup>-4</sup>
Cl	0.12x10 <sup>-4</sup>	FO <sub>2</sub>	0.11x10 <sup>-4</sup>

FIGURE 7

FIGURE 7. Composition of Gas Phase at 900°C with O<sub>2</sub>/0.11 vol% C<sub>2</sub>H<sub>3</sub>Cl<sub>2</sub>F and O<sub>2</sub>/0.11 vol% NF<sub>3</sub> system. (10 ppm of H<sub>2</sub> added to each system considering the hydrocarbon impurities in the oxygen).

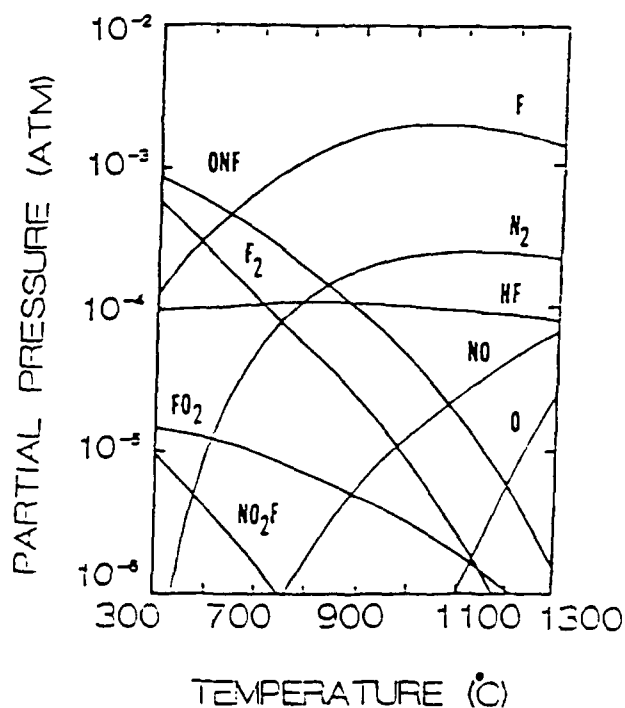


FIGURE 8

FIGURE 8. Equilibrium partial pressure in N-F-O-H system vs. temperature. (Total pressure = 1 atm, NF<sub>3</sub> = 0.044 vol% and H<sub>2</sub> = 0.005 vol%).

Guided by these programs, we then took the most attractive sources and committed these to the experimental studies.

The analytic work involving the determination of the F concentration in depth in the oxide and its role on mechanical properties was included as part of all the experimental studies. Data from SIMS was obtained from many samples. A sample of the different resulting F concentration from both sources can be seen from the below FIGURES 9 and 10:<sup>(3)</sup>

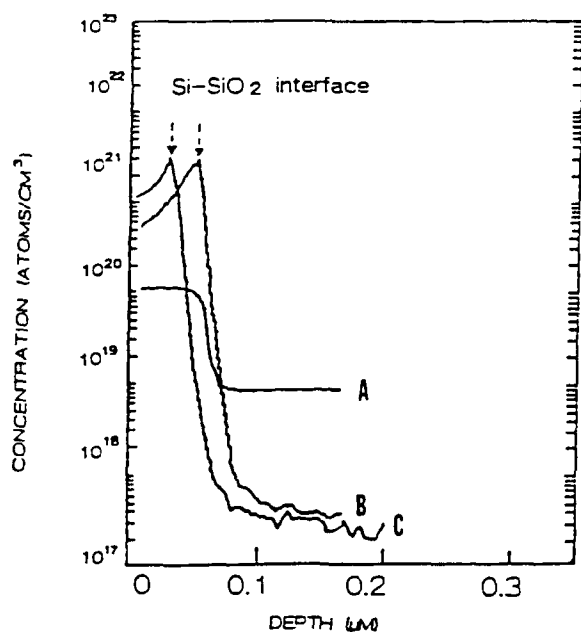


FIGURE 9

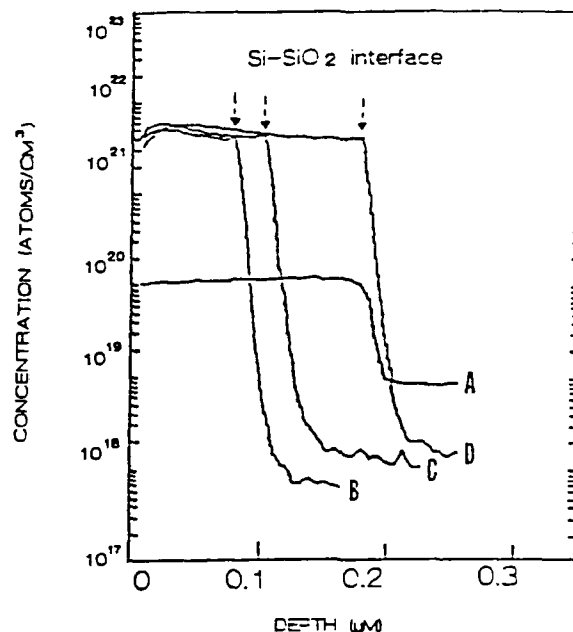


FIGURE 10

FIGURE 9. Fluorine and oxygen profiles of an oxide grown at 800°C with 0.011 v/o  $C_2H_3Cl_2F$  in  $O_2$ . A, oxygen profile; B, 8h and C, 2h.

FIGURE 10. Fluorine and oxygen profiles of oxides grown in different amounts of  $NF_3$  addition at 900°C. A, oxygen profiles; B, 2h 0.011%  $NF_3$ ; C, 2h 0.033%  $NF_3$ ; D, 4h 0.022%  $NF_3$ .

The above is illustrative of the "peaked" concentration (FIGURE 9) when the presence of  $H_2$  in the source allows  $H_2O$ -F replacement reaction to occur.

FIGURE 10 shows an example of the "saturated" level concentration using the  $NF_3$  source and very dry conditions. Further details of this work and particularly the work in which the Fluorine was included as pulses during oxidation processes will be part of the Lehigh Thesis of Dimitrios Kouvatsos.<sup>(12)</sup>

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2. "Oxidized CVD  $\text{Si}_3\text{N}_4$  in Fluorine Ambient", U.S. Kim and R.J. Jaccodine, Extended Abstracts of Electrochemical Society Meeting, Abstract 216, Los Angeles, CA, May 1989.
3. "The Effect of Fluorine Additive in the Oxidation of Silicon", U.S. Kim, C.H. Wolowodiuk, R.J. Jaccodine, F.A. Stevie, and P.M. Kohora, to be published in J. Electrochem. Society.
4. "Effect of  $\text{NF}_3$  Addition on Point Defect Generation at the Oxidizing Interface", U.S. Kim, R.J. Jaccodine, F.A. Stevie, and T. Kook, to be published in J. Electrochem. Society.
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10. " $\text{SiO}_2$  Film Stress Thickness Dependence for Dry and Fluorinated Oxides and Relevant Fluorinated Effects", D. Kouvatsos, P.J. Macfarlane, R.J. Jaccodine and F.A. Stevie, presented at the 180th Meeting of the Electrochemical Society, Phoenix, AZ, October 13-18, 1991.



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#### Education

1947	B.S.	U.S. Naval Academy
1951	M.S.	Physics, Steven Institute of Technology
1957	Ph.D.	Physics, Notre Dame University

#### Positions

Bell Telephone Laboratories (1958-1981)	
1959-61	Member of Technical Staff
1961-68	Supervisor on wide range of crystal growth related studies
1972-78	Department Head of MOS Technology
1978-81	Department Head of Bipolar Technology
1981-	Fairchild Professor of Solid State Materials, Lehigh University

#### Research Activity

Stacking faults and distortion behavior  
Integrated circuits and devices  
Solid state diffusion  
Oxygen precipitation  
Imperfection studies  
IEEE Gel Task Force  
Bipolar technology  
Ion implantation  
MOS technology  
Director, SRC Packaging Program

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Sigma Xi

Dr. Donald R. Young

Education

1942 B.S.	Utah State Major-Physics; Minor-Mathematics
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Positions

1942-45	Massachusetts Institute of Technology Radiation Laboratory
1945-49	Massachusetts Institute of Technology Laboratory for Insulation Research
1949-86	International Business Machines
1972-73	Sabbatical leave as visiting Mackay Lecturer Electrical Engineering Department University of California
1980-81	Sabbatical leave at Institut fur Halbleitertechnik Technische Hochschule, Aachen, Federal Republic of Germany. U.S. Senior Scientist Award, Alexander von Humboldt Foundation
1982-86	Adjunct Professor, Lehigh University, Bethlehem, PA (with exception of 1984)
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Chairman, 1982 Gordon Conference on MIS Systems  
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